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EVALUATION OF A RAPID TEST FOR AVAILABLE ALKALI DETERMINATION IN FLY ASHES

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Mineral Processing Laboratory

January 1983

For presentation at the First International Conference on the Use of Fly Ash, Silica Fume, Slag and Other Mineral By-Products in Concrete, Montebello, Canada, July 31 - Aug. 5, 1983 and for publication in an ASTM Journal, Cement, Concrete and Aggregates

Project MRP-3.6.0.0.65
Waste Minerals as Supplement to Portland Cement

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EVALUATION OF A RAPID TEST FOR AVAILABLE ALKALI DETERMINATION IN FLY ASHES

by

A.A. Winer* and V.M. Malhotra**

ABSTRACT

A rapid method for available alkali in fly ash has been evaluated. Fourteen samples of fly ash, obtained from producers of fly ash in Canada have been subjected to both the ASTM Standard test and the rapid methods. The procedure for the rapid method is simple and can be completed within 30 minutes compared to 28 days for the ASTM procedure. A statistical analysis shows that a highly significant correlation exists between the two methods and the precision of the rapid method is at least as good as the ASTM method.

When results from all previous correlation investigations for the ASTM versus rapid methods are combined with those from the present investigation, the regression line obtained is highly significant at the 99 per cent level. The correlation coefficient is 0.97.

In preliminary testing for sodium and potassium in the filtrate leached from fly ash by sulphuric acid interference from sulphate is found to be negligible.

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INTRODUCTION

Interest in fly ash had been stimulated in Saskatchewan in 1960 because of the proposed building of concrete dams, and because fly ash collection equipment had been installed at the lignite coal burning power station at Estevan, Saskatchewan.

Because of the short ash collecting cycle, approximately one hour, and lack of storage facility, a rapid test for available alkali became imperative if fly ash was to be used and expensive storage construction was to be avoided.

In previous investigations by the Saskatchewan Research Council (1) and CANMET (2) the results of a rapid method and the ASTM Standard test (C311-77) for available alkali in a Saskatchewan fly ash, were compared. The results showed a significant correlation (2). However the number of tests was limited, and all samples came only from one Saskatchewan source.

The rapid test was further investigated at the University of Saskatchewan for interferences which were said to suppress the results by the rapid technique. The sulphate ion was considered to be the major cause of interference (3).

This study was initiated to obtain additional data for the rapid test and a total of 14 fly ashes from Canadian sources were investigated.

INITIAL DEVELOPMENT OF THE RAPID METHOD

After a preliminary investigation at the Saskatchewan Research Council, based on previous experience in leaching fly ash, a rapid method was standardized. Five gram samples of fly ash were treated with 100 mL of sulphuric acid (5 per cent solution by mass) and stirred for 5 minutes at 20°C (1). Filtered aliquots of the suspension were analyzed using a spectrophotometer with a flame adaptor. A good statistical correlation was found between results for fly ash analyzed by the ASTM method (ASTM C311-77)and the rapid method. The rapid method was completed in less than 45 minutes per test. It should be noted that all samples of fly ash in the

above study were derived from one source, the lignite coal used at the Estevan, Saskatchewan power station. A further study by the University of Saskatchewan indicated that sulphate was considered to be an interference in the rapid method by depressing the actual values of the leached sodium. Other ions did not interfere to the same degree (3). Discrepancy in reproductibility of results was also traced, in part, to particle segregation due to particle size and density variations (1).

In view of the nature of the problems noted above it was decided to test fly ashes from all the major producers in Canada using instrumentation which is said to avoid the effect of sulphate*. These results would then be compared with the results from tests by the ASTM C311-77 standard method.

Advantages of the rapid available alkali test for fly ash are noted below. This test would:

(a) reduce the cost of analysis,

(b) reduce the cost or necessity for building storage facilities for fly ash,

(c) increase the desirability of using fly ash in the concrete industry, therefore increasing conservation of materials and energy.

CURRENT LABORATORY INVESTIGATION

Samples

Bulk samples of fly ash were collected by CANMET. These were representatively sampled and precautions taken so that the fines, suspected to contain a major portion of the alkali were included in the sample. Segregation of the fly ash particles had previously been found to occur (1). Samples of five hundred grams each were tested by the rapid and the ASTM methods. The chemical analyses of the fly ashes are shown in Table 1.

Available Alkali by the ASTM Method**

The standard test has been virtually unchanged for many

*Correspondence from Saskatchewan Research Council

** All testing was performed by Saskatchewan Research Council under CANMET Contract No. 03SQ.23440-1-9095.

years and is designated as ASTM C311-77 (4). Essentially, a fixed amount of fly ash is mixed with calcium hydroxide and water, and stored in a vial at 38°C for 28 days. At the end of this period, the sodium oxide and potassium oxide are determined in the solution by a flame photometer. The result is reported as equivalent sodium oxide per cent*.

Available Alkali by the Rapid Procedure**

The fly ash was representatively sampled using a splitter. Five grams were taken from a split fraction and added to 100 mL of 5 per cent sulphuric acid in a 250-mL beaker. The mixture was stirred at room temperature for 5 minutes at a speed just sufficient to keep the ash in suspension. The mixture was filtered and washed with warm distilled water. The filtrate was made up to volume in a 250 m volumetric flask. Each fly ash was tested in duplicate.

Sodium and potassium were determined by both flame emission† and atomic-absorption†† spectrometry. No discrepancy was observed between results obtained using the two techniques. Calibration curves were obtained by both techniques, from zero to the highest concentration of the chosen standard.

Interference from sulphate was found to be negligible during preliminary testing†††.

TEST RESULTS AND THEIR ANALYSIS

The analytical results obtained for the 14 fly ash samples are shown in Table 2. A statistical analysis of the results is shown in Tables 3 and 4.

The line of best fit based on a linear regression analysis is shown in Figure 1.

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*Na_2O equiv = Na_2O, % + 0.658 x K_2O, %

**All testing by Saskatchewan Research Council under CANMET Contract No. 03SQ.23440-1-9095

†1 L Model 443 Flame Photometer

††Perkin-Elmer Model 2380

†††Correspondence from Saskatchewan Research Council

DISCUSSION OF TEST RESULTS

Sulphate Interference

Initially, in the rapid procedure using a flame photometer, it was suspected that sulphate was suppressing the results (3). In the present accelerated method, sodium and potassium were determined using flame emission and atomic absorption spectrometry. Preliminary testing found negligible interferences from sulphate*.

Comparison of Results between the ASTM and the Rapid Methods

The correlation of results for the ASTM vs Rapid test is highly significant. The correlation coefficient is 0.97 and the level of significance 99.9 per cent (Tables 3,4).

The results for the rapid method are consistently lower than for the ASTM method up to about one per cent available alkali. Beyond this value the results from both methods coincide very well. The conforms essentially to the observations made in previous studies (1,2). The reason for this anomaly is not known at present. However, the regression analysis as shown by the scatter diagram indicates a distinct and highly significant relationship between the two methods.

The rapid method has a precision at least as good as that for the ASTM method (Table 3). For some results, the rapid method gave better precision.

Although more samples with available alkali in the range between 0.5 and 2.5 per cent would have been preferable, the present investigation would suggest that an excellent correlation exists between the two methods for samples containing 0.5 per cent and greater available alkali**.

Variation in Results of the Rapid Method

In order to verify the rapid procedure, a further check was made on the rapid method in the same laboratory with the same analyst. All 14 samples were again representatively sampled and

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*Correspondence from Saskatchewan Research Council

**ASTM Standard specification for fly ash, ASTM C618-80: Maximum allowable available alkali 1.5 per cent

analyzed for available alkali by the rapid procedure. Only one test was performed on each sample. These tests were done approximately 30 days after the initial testing in duplicate. The results of these tests are shown in Table 5. The differences are not considered significant.

Composite Data from Previous Investigations

In this investigation only presently available samples from Canadian sources of fly ash were used and consequently only a few data points were obtained in the medium and higher range of available alkali content. To redress this, it was decided to carry out a regression analysis on all the available data obtained from the current and previous investigations. The results of the analysis are shown in Figures 2 and 3.

The correlation between the ASTM and rapid methods, shows a statistically high level of significance. The largest scatter of results noted previously, is in the extreme end of the graph, i.e., for samples with very low content of available alkali. For practical purposes, this is not greatly significant.

CONCLUSIONS

1. The rapid method is simple and takes less than 45 minutes to complete. In the technique used, negligible interference was found due to sulphate.
2. The results of the rapid test correlate significantly with the ASTM method.
3. Below about 0.5 per cent available alkali, the absolute numerical results for the rapid method were consistently lower than those for the ASTM method. However, the correlation was still statistically significant.
4. Using data obtained from previous studies done from 1961 to 1982, the line of best fit obtained from the regression analysis was highly significant at the 99 per cent level.

ACKNOWLEDGEMENT

Financial support for this investigation was provided by CANMET to ASCOR under Contract No. 03SQ.23440-1-9095. CANMET Scientific Authority for the project was V.M. Malhotra. Principal investigator at ASCOR was Mr. A.A. Winer.

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3. Orr, R.C.T. "Problems on accelerated tests for available alkali in fly ash"; Bachelor of Science Thesis, Faculty of Engineering, University of Saskatchewan; April, 1962.

4. "Standard methods of sampling and testing fly ash or natural pozzolans for use as a mineral admixture in portland cement concrete"; ASTM C311-77; ASTM, Philadelphia, Pa.; 1977.

Table 1 - Summary of Test Data on Some Physical and Chemical Properties of 14 Canadian Fly Ashes*

Fly Ash No.	Weight Percent ± 1σ												
	Al as Al_2O_3	Fe as Fe_2O_3	Ti as TiO_2	Ca as CaO	Mg as MgO	S as SO_3	Na as Na_2O	K as K_2O	Si as SiO_2	Total as Oxides	LOI	Magnetic Portion**	% of Water Soluble Fraction
1	22.3 ± 0.5	4.1 ± 0.1	1.01 ± 0.01	13.6 ± 0.4	1.58±0.04	0.2 ± 0.1	0.27 ± 0.03	1.02±0.06	54.8±0.4	98.9	0.26	≤1	4±0.5
2	23.1 ± 0.5	3.7 ± 0.1	0.78 ± 0.01	13.0 ± 0.4	1.17±0.04	0.2 ± 0.1	2.19 ± 0.03	1.26±0.06	57.6±0.4	103.0	0.15	≤1	2±0.5
3	21.0 ± 0.5	3.5 ± 0.1	0.50 ± 0.01	11.6 ± 0.4	0.71±0.04	≤0.1	1.68 ± 0.03	1.51±0.06	56.4±0.4	97.0	0.61	≤1	2±0.5
4	22.7 ± 0.5	3.7 ± 0.1	0.60 ± 0.01	8.4 ± 0.4	0.75±0.04	≤0.1	2.36 ± 0.03	1.02±0.06	57.4±0.4	97.0	0.10	≤1	4.5±0.5
5	23.7 ± 0.5	4.4 ± 0.1	0.94 ± 0.01	19.2 ± 0.4	3.96±0.04	0.6 ± 0.1	0.54 ± 0.03	2.41±0.06	57.9±0.4	105.6	0.13	≤1	7±0.5
6	20.4 ± 0.5	5.4 ± 0.1	0.60 ± 0.01	12.2 ± 0.4	1.38±0.04	0.1 ± 0.1	0.84 ± 0.03	1.93±0.06	52.6±0.4	95.5	0.12	≤1	1±0.5
7	20.8 ± 0.5	4.1 ± 0.1	0.97 ± 0.01	20.0 ± 0.4	3.13±0.04	0.2 ± 0.1	5.66 ± 0.07	1.14±0.06	40.7±0.4	96.7	0.83	≤1	2.5±0.5
8	20.8 ± 0.5	3.8 ± 0.1	0.87 ± 0.01	18.6 ± 0.4	2.42±0.04	≤0.1	5.80 ± 0.07	1.45±0.06	38.1±0.4	91.9	0.34	≤1	3.5±0.5
9	22.7 ± 0.5	16.5 ± 0.8	1.01 ± 0.01	4.6 ± 0.4	0.64±0.04	0.5 ± 0.1	0.54 ± 0.03	2.0 ±0.06	44.6±0.5	93.1	5.9	85.±1.	3.5±0.5
10	21.2 ± 0.5	7.1 ± 0.8	0.81 ± 0.01	6.6 ± 0.4	0.88±0.04	0.1 ± 0.1	0.4 ± 0.03	1.14±0.06	51.9±0.5	90.1	5.3	69.±1.	2.5±0.5
11	13.6 ± 0.5	38.5 ± 0.8	0.51 ± 0.01	1.81 ± 0.04	0.14±0.01	0.6 ± 0.1	0.11 ± 0.01	1.93±0.06	34.9±0.4	91.4	0.11	96.±1.	1.5±0.5
12	13.6 ± 0.5	42.4 ± 0.8	0.56 ± 0.01	1.22 ± 0.04	0.06±0.01	0.4 ± 0.1	0.09 ± 0.01	1.26±0.06	31.7±0.4	91.3	2.0	87.±1.	1 ± 0.5
13	20.8 ± 0.5	24.4 ± 0.8	0.76 ± 0.01	0.94 ± 0.04	0.12±0.01	0.6 ± 0.1	0.34 ± 0.03	1.63±0.06	46.7±0.4	96.3	0.53	94.±1.	1.5±0.5
14	18.0 ± 0.1	19.2 ± 0.2	0.74 ± 0.01	0.76 ± 0.5	0.75 ±0.04	0.99±0.5	0.39 ± 0.03	2.93 ±0.05	44.7±0.2	88.5	6.25		1 ± 0.5

*Chemical Analysis by Joshi and Consultants, Calgary, Alberta

**This is the amount of the sample attracted to a magnetic. It does not indicate the amount of magnetite fraction in ash.

Table 2 - Results of Available Alkali by the ASTM vs Rapid Method*

Fly Ash Sample No.	Equivalent Na_2O %					
	ASTM Method			Accelerated Method		
	(1)	(2)	Avg.	(1)	(2)	Avg.
1	0.16	0.22	0.19	0.013	0.013	0.013
2	0.78	0.79	0.79	0.057	0.057	0.057
3	0.39	0.36	0.38	0.17	0.14	0.16
4	0.40	0.41	0.41	0.10	0.10	0.10
5	0.31	0.33	0.32	0.12	0.11	0.12
6	0.48	0.47	0.48	0.012	0.012	0.012
7	0.36	0.36	0.36	0.083	0.082	0.083
8	1.4	1.40	1.40	1.2	1.3	1.25
9	2.0	2.3	2.15	2.1	2.0	2.05
10	0.35	0.35	0.35	0.079	0.081	0.080
11	0.30	0.30	0.30	0.050	0.051	0.051
12	0.33	0.33	0.33	0.045	0.045	0.045
13	0.33	0.34	0.34	0.026	0.025	0.026
14	0.52	0.49	0.51	0.091	0.090	0.091

*Duplicate analysis for all samples

Table 3 - Available Alkali in Fly Ash: ASTM vs Rapid Method

Method	Grouping Variable Level	Total Frequency	Mean	Standard Deviation	St. Err of Mean	Coeff. of Variation*	Range
ASTM							
	Sample #1	2	.190	.042	.0300	.22330	.060
	#2	2	.785	.007	.0050	.00901	.010
	#3	2	.375	.021	.0150	.05657	.030
	#4	2	.405	.007	.0050	.01746	.010
	#5	2	.320	.014	.0100	.04419	.020
	#6	2	.475	.007	.0050	.01489	.010
	#7	2	.360	.000	.0000	.00000	.000
	#8	2	1.400	.000	.0000	.00000	.000
	#9	2	2.150	.212	.1500	.09867	.300
	#10	2	.350	.000	.0000	.00000	.000
	#11	2	.300	.000	.0000	.00000	.000
	#12	2	.330	.000	.0000	.00000	.000
	#13	2	.335	.007	.0050	.02111	.010
	#14	2	.505	.021	.0150	.04201	.030
RAPID							
	Sample #1	2	.013	.000	.0000	.00000	.000
	#2	2	.057	.000	.0000	.00000	.000
	#3	2	.155	.021	.0150	.13686	.030
	#4	2	.100	.000	.0000	.00000	.000
	#5	2	.115	.007	.0050	.06149	.010
	#6	2	.012	.000	.0000	.00000	.000
	#7	2	.083	.001	.0005	.00857	.001
	#8	2	1.250	.000	.0000	.00000	.000
	#9	2	2.050	.071	.0500	.03449	.100
	#10	2	.080	.001	.0010	.01768	.002
	#11	2	.051	.001	.0005	.01400	.001
	#12	2	.045	.000	.0000	.00000	.000
	#13	2	.026	.001	.0005	.02773	.001
	#14	2	.091	.001	.0005	.00781	.001

*Coefficient of variation is not expressed as a percentage

Table 4 - Analysis of Variance for the Test Data

Dependent Variable ..... ASTM

All Data Considered as a Single Group

Multiple R 0.9668

Std. Error of Est. 0.1392

Multiple R-Square 0.9347

Analysis of Variance

	Sum of Squares	DF	Mean Square	F Ratio
Regression	3.5561	1	3.5561	183.436
Residual	0.2326	12	0.0194	

Variable	Coefficient	Std. Error	Std. Reg Coeff	T
Intercept	0.33355			
Rapid	0.87490	0.06511	0.967	13.544

Table 5 - Variation of Results for Available Alkali in Fly Ash by the Rapid Method

CANMET Sample No.	Available Alakli, Per Cent				Difference (Run 2 - Run 1)
	Run 1			Run 2 (1 test)*	
	Test 1	Test 2	Average (1,2)		
1	0.013	0.013	0.013	0.016	0.003
2	0.057	0.057	0.057	0.057	0.00
3	0.17	0.14	0.16	0.130	-0.03
4	0.10	0.10	0.10	0.110	0.01
5	0.12	0.11	0.12	0.094	-0.026
6	0.012	0.012	0.012	0.012	0.00
7	0.083	0.082	0.083	0.081	-0.002
8	1.2	1.3	1.25	1.10	-0.15
9	2.1	2.0	2.05	2.20	0.15
10	0.079	0.081	0.080	0.077	-0.003
11	0.050	0.051	0.051	0.057	0.006
12	0.045	0.045	0.045	0.049	0.004
13	0.026	0.025	0.026	0.031	0.005
14	0.091	0.090	0.091	0.091	0.000

*Run 2 - Tested approximately 30 days after completion of Run 1

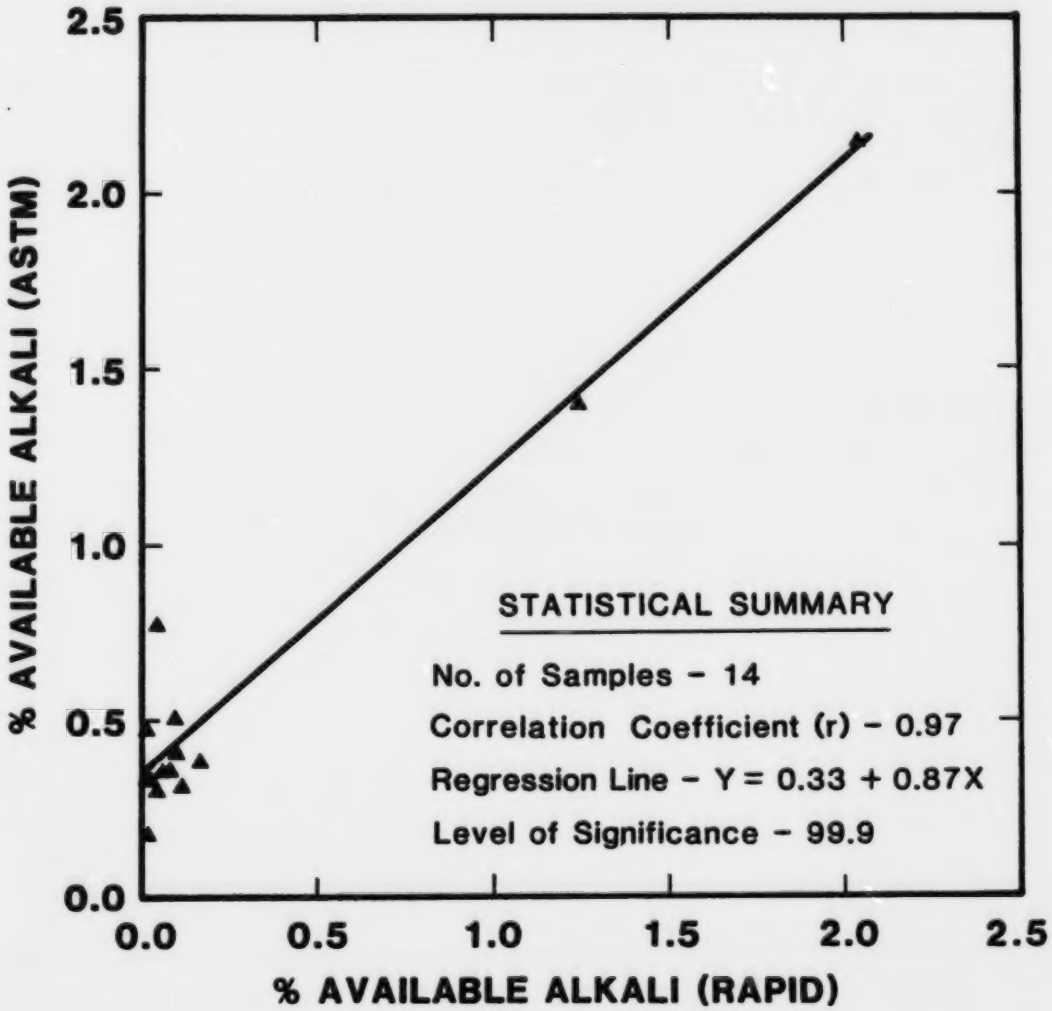

Fig. 1 - Scatter Diagram and Statistical Summary for Available Alkali - Current Investigation

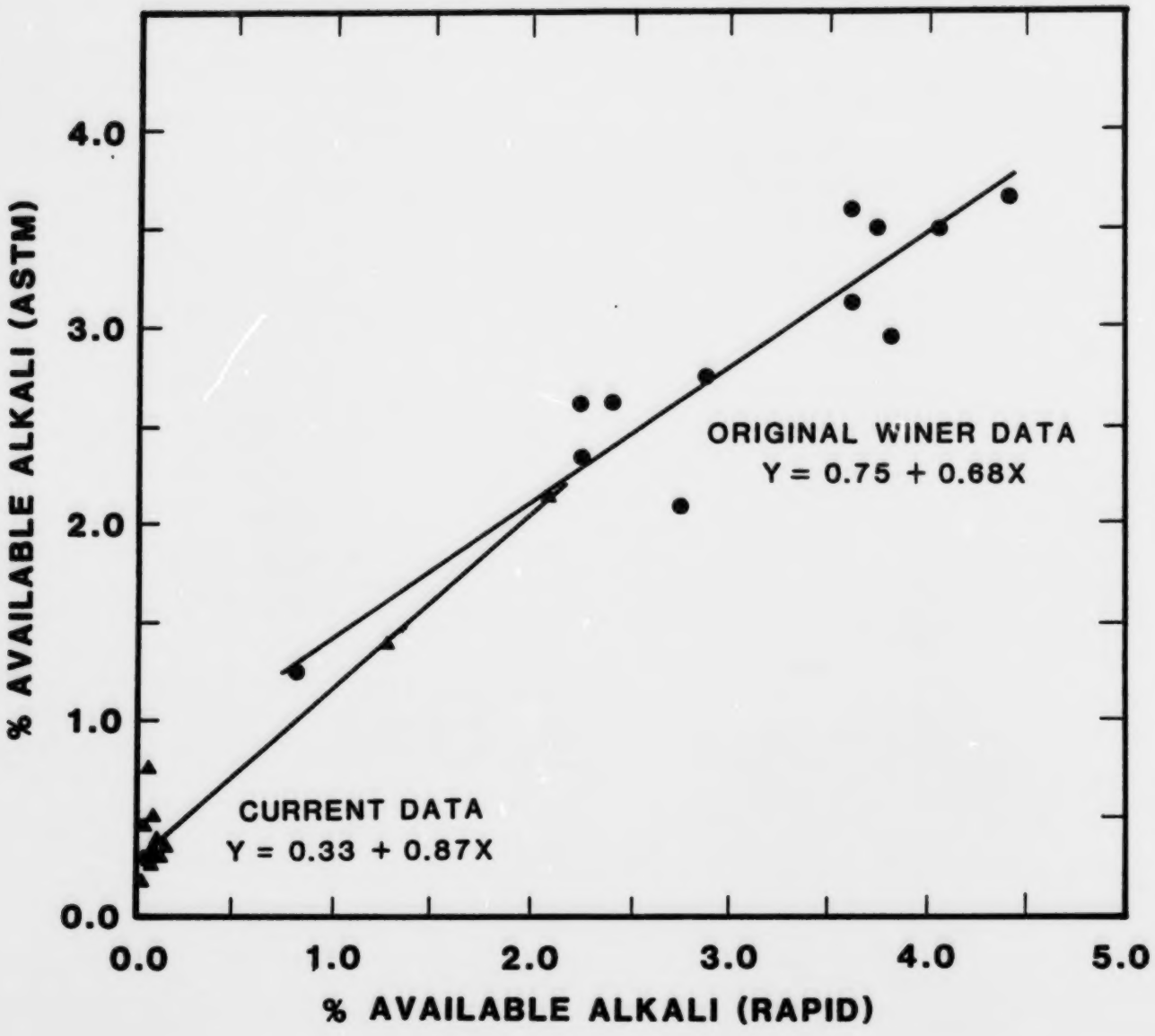

Fig. 2 - Scatter Diagram and Statistical Summary for Available Alkali: Original Winer Data and Data From Current Investigation

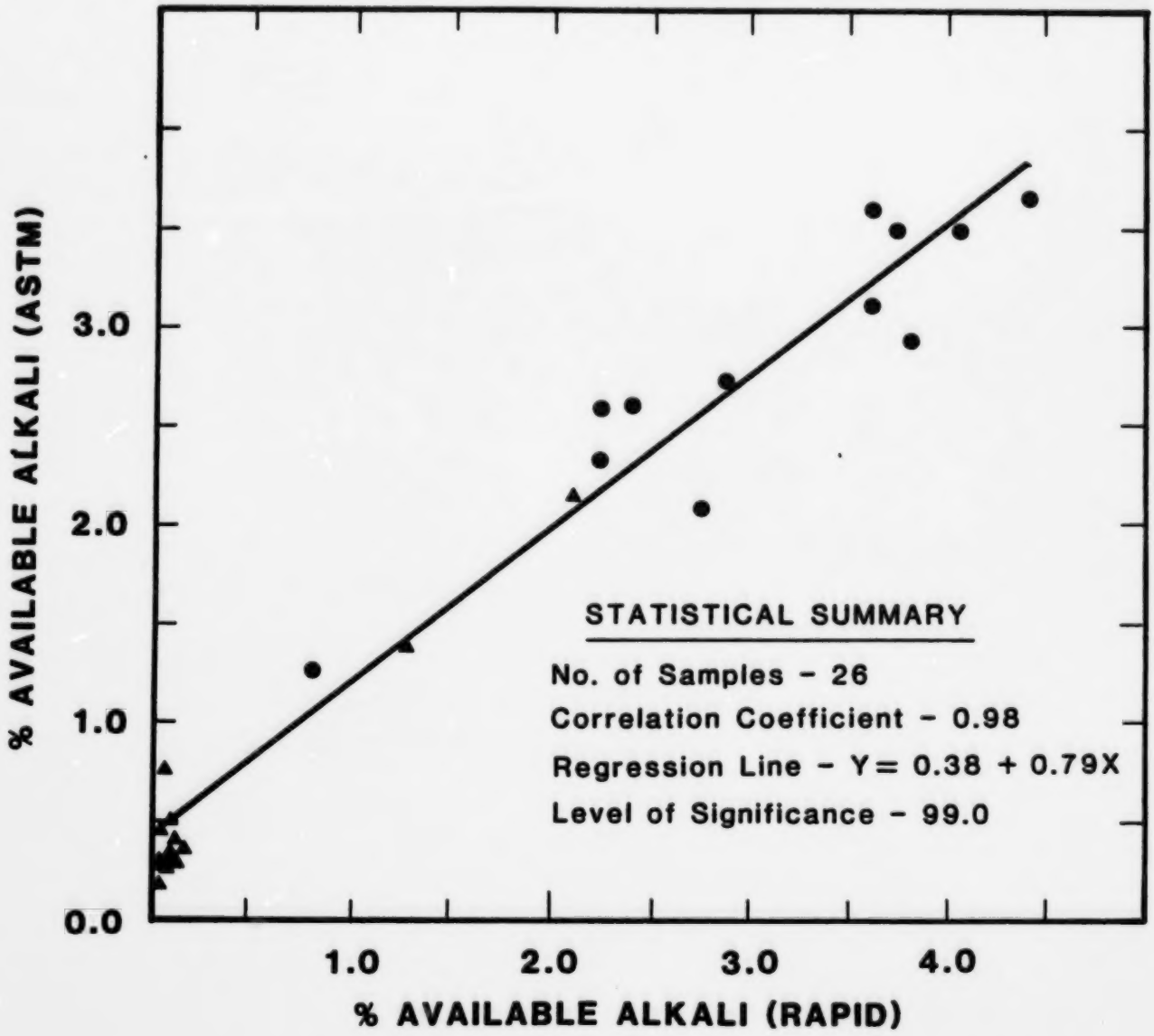

Fig. 3 - Scatter Diagram and Statistical Summary for the Combined Data

POOR

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